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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US90/01635 <b>(22) International Filing Date:</b> 30 March 1990 (30.03.90)  <b>(30) Priority data:</b> 330,497                      30 March 1989 (30.03.89)      US 497,648                      23 March 1990 (23.03.90)      US  <b>(71) Applicant:</b> JAMES RIVER PAPER COMPANY, INC. [US/US]; 28 Gaylord Street, South Hadley, MA 01075 (US).  <b>(72) Inventors:</b> FOLEY, Diane, M. ; 262 Bridge Street, Northampton, MA 01060 (US). BENNETT, Everett, W. ; 210 Park Street, Easthampton, MA 10127 (US). SLIFKIN, Sam, C. ; 26 Prospect Street, South Hadley, MA 01015 (US).		<b>(74) Agents:</b> STEPNO, Norman, H. et al.; Burns, Doane, Swecker & Mathis, George Mason Building, Washington & Prince Streets, P.O. Box 1404, Alexandria, VA 22313-1404 (US).  <b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> A NEAR INFRARED LASER ABSORBING COATING AND METHOD FOR USING SAME IN COLOR IMAGING AND PROOFING  <b>(57) Abstract</b>  A laser imaging material which can be effectively employed for color printing and proofing comprises a near infrared transparent support film which has a near infrared absorbing layer thereon. The absorbing layer contains at least one sensitizer which is absorbent at a desired near infrared laser output wavelength and a decomposable binder. Laser radiation at the desired wavelength which acts upon the absorbing sensitizer causes rapid partial decomposition of the binder into gaseous and non-gaseous products. The rapid expansion of the heated gases causes ablation of inert materials from the surface of said layer onto a receptor sheet thus producing an imaged film (i.e., the laser imaging donor material) and a color print or proof (i.e., the receptor sheet) of reversed sign to the imaged donor material.		

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A NEAR INFRARED LASER ABSORBING COATING AND  
METHOD FOR USING SAME IN COLOR IMAGING AND PROOFING

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BACKGROUND OF THE INVENTION

The present invention relates to a laser imaging material which includes a near infrared laser absorbing coating composition and color imaging and proofing methods using the material.

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The laser induced ablative imaging of a material having an imaging layer thereon is known in the art. Ablative imaging is a material transfer process in which laser radiation causes rapid local changes in the imaging layer thereby causing the loss of material, for example, ejecting material from the layer. Ablation as described herein is distinguished from other material transfer techniques in that some degree of a chemical (i.e., bond breaking) rather than a completely physical (i.e., melt/flow, evaporation, sublimation) change causes the transfer and in that an essentially complete transfer of material rather than partial transfer occurs.

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In order for ablation to occur, one or more of the components in the imaging layer must effectively absorb laser light. At short wavelengths (i.e., less than 300 nm), many organic materials are strongly absorbing. Therefore, 193 nm and 248 nm excimer lasers are commonly used in laboratory research into the photoablation of polymers.

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However, due to the economics involved in commercial practice, the use of visible (380-760 nm) and near IR (760-3000 nm) lasers is much more desirable. Unfortunately few polymers have significant

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absorption in the visible and fewer still absorb in the near IR. This deficiency has been overcome by adding dispersed or soluble materials absorbing at the desired wavelengths to the polymers. See, for example, the  
5 discussion in the T.J. Chuang et al article in Applied Physics, Vol. 45, pgs. 277-288 (1988) which is incorporated herein by reference.

This strategy is often used in information recording with the visible diode lasers emitting at  
10 wavelengths of 760 to 850 nm. See, for example, U.S. Patents 4,415,621; 4,446,233; 4,582,776; and 4,809,022 and the N. Shimadzu et al article in the Journal of Imaging Technology, Vol. 15, No. 1, page 19 (1989).

Currently available power densities and dwell  
15 times used in information recording for optical disks are sufficient to cause polymer melting and flow, but insufficient to generate the extreme force of polymer decomposition necessary to transfer large amounts of inert materials to an adjacent surface. One laser in  
20 commercial practice which does supply sufficient power density (about  $10^6$  watts/cm<sup>2</sup> vs. about  $10^3$  watts/cm<sup>2</sup> for laser diodes) is the Crosfield Datrax Nd:YAG laser emitting at 1064 nm. Ablation imaging at 1064 nm has been described. Infrared absorbers which are used in  
25 absorbing layers for use with, for example, a near IR 1064 nm laser include black body materials such as: graphite, see, for example, U.S. Patents 4,702,958 and 4,711,834; carbon black, see, for example, U.S. Patent 4,588,674; and a combination of graphite with small  
30 amounts of Cyasorb IR 165, 126, or 99, as in Great Britain Patent 2,176,018A.

In the absorbing layer, the absorbers are usually dispersed in a commercially available polymeric binder including a self oxidizing binder such as

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nitrocellulose, or a non-self oxidizing binder such as ethylcellulose, acrylic resins, polymethylmethacrylate, polymethacrylate, polystyrene, phenolic resins, polyvinylchloride, vinyl chloride/vinyl acetate copolymers, cellulose acetate butyrate, and the like. In measurements by differential scanning calorimetry (DSC), each of the above polymeric binders has a decomposition temperature which is greater than 200°C, except for nitrocellulose which undergoes thermal decomposition at about 180°-210°C.

Because the graphite and carbon black absorbers are highly absorbing throughout the IR, visible and UV regions, the resulting films are useful only when a black image is desired.

In the past, such laser imaging materials have been used as an intermediate film in printing plate production within the printing industry. In this method, the materials which are imaged with a laser provide a negative which can be used as a master to expose plates for printing. A receptor sheet which receives the inert materials from the coating upon ablation, is thus a reversal image or positive which can be used as a black and white proof or print. However, for the reasons discussed above the previously described materials are entirely ineffective for color imaging.

Therefore, the need still exists for a cost effective laser ablatable coating which is inherently substantially colorless in the visible region and thus, can be effective in areas such as color proofing in the printing industry and other laser-addressable ablation transfer color printing systems.

Accordingly, it is an object of the present invention to provide a laser-ablatable coating layer

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which can be tuned to a variety of laser output wavelengths by choice of the appropriate sensitizers to absorb the radiation and also cause the decomposition leading to ablation and which contains additional materials depending on the function of the product which are transferred during the ablation process to a receiver sheet. The imaged film, the receiver sheet or both may be of interest to the final product.

Further, it is an object of the present invention to sensitize the coating layer to laser wavelengths sufficiently different from the visible region to allow for substantially transparent coatings to which visible colorants may be added without affecting their color purity. An example of such a laser in commercial practice is a Nd:YAG laser emitting light at 1064 nm employed in the imaging hardware of a Crosfield Datrax 765.

It is still a further object of the present invention to provide a near infrared (IR) sensitive ablative layer which is transparent in the visible range so that ultraviolet (UV), visible, and/or near IR absorbing dyes and/or pigments may be added to the coating layer.

These and further objects will become apparent from the specification and claims that follow.

#### SUMMARY OF THE INVENTION

In accordance with the foregoing objectives, the present invention relates to a near infrared absorbing coating, a near infrared ablatable imaging material which uses the coating and a method for providing both a positive or negative color print or proof and a negative or positive imaged color film or

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intermediate master using the laser imaging material by means of laser induced ablation transfer.

5 In particular, the coating or coated layer of the present invention comprises at least one sensitizer which absorbs at the wavelength of the desired laser output in the near infrared region of 760 nm to 3,000 nm, and at least one decomposable binder. The at least one sensitizer is present in an amount effective to allow the rapid partial decomposition of the at least one binder when the at least one sensitizer interacts with laser light. The decomposable binder comprises those polymeric materials which undergo rapid acid catalyzed decomposition, preferably at temperatures less than 200°C. The coating may also, optionally, 10 contain materials which are non-absorbing at the wavelength of the desired laser output and/or non-decomposing as well as optimal amounts of commercially available binders which are not decomposable binders in the imaging process. In a preferred embodiment, the 15 coating comprises at least one near infrared sensitizer, at least one decomposable binder, and at least one hydrogen atom donating material. 20

In another aspect of the present invention, a near infrared laser ablation transfer imaging material is provided. This material comprises a near infrared transparent support film bearing a layer of near infrared absorbing coating. The material can be effectively employed for color imaging. 25

Upon exposure to laser light, the absorbing sensitizer interacts with the laser light and causes rapid partial decomposition of the binder to gaseous and non-gaseous products. The rapid expansion of the heated gases causes ablation of the exposed coating 30

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layer to a receptor sheet providing a reverse of the imaged color film (i.e., a color print or proof).

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates one embodiment of the method of the present invention employing near infrared transparent supports.

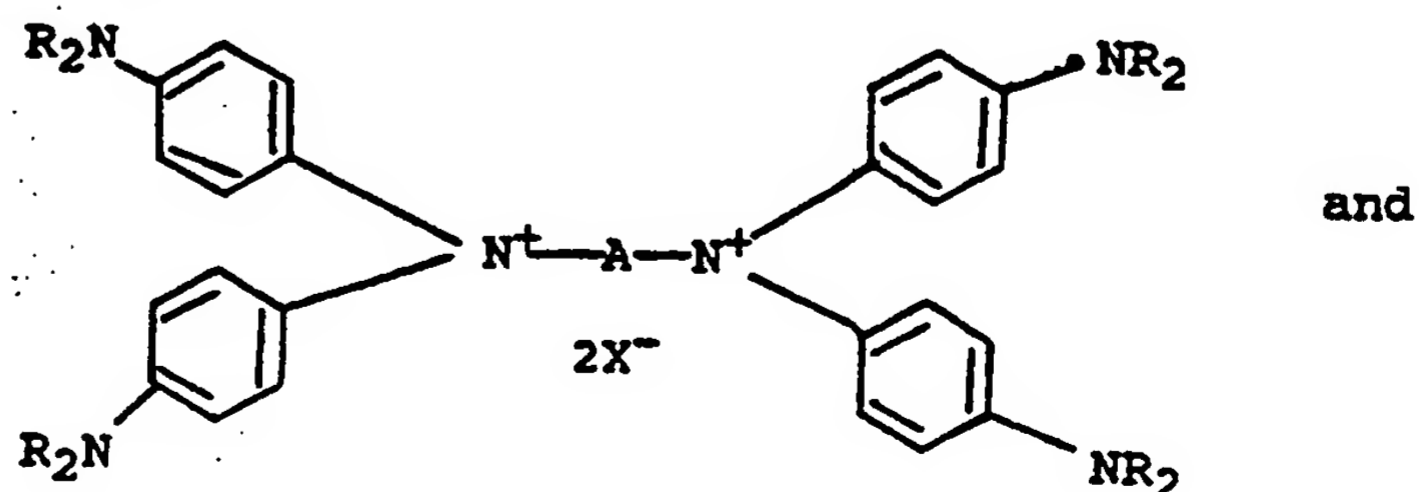
Fig. 2 illustrates a second embodiment of the method of the present invention employing near infrared non-transparent supports.

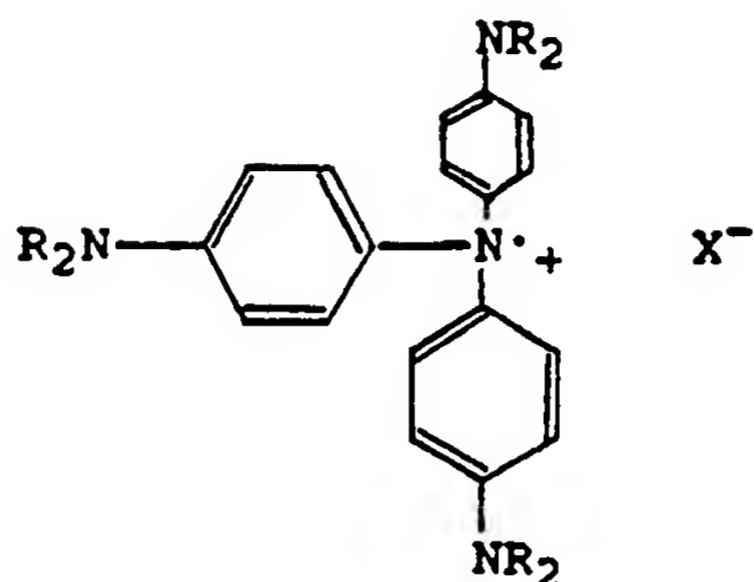
#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The coating composition of the present invention comprises a solution or dispersion containing at least one near infrared sensitizer and a decomposable binder.

The absorbing sensitizers which can be used in the present invention include any material which can absorb at a desired wavelength for a particular near infrared laser output and which preferably can initiate acid formation. In particular, when visibly transparent coatings are required, for example, substituted aromatic diamine dication-type sensitizers absorbing at 1064 nm and having counterions derived from strong acids are preferred. Examples of such sensitizers are:

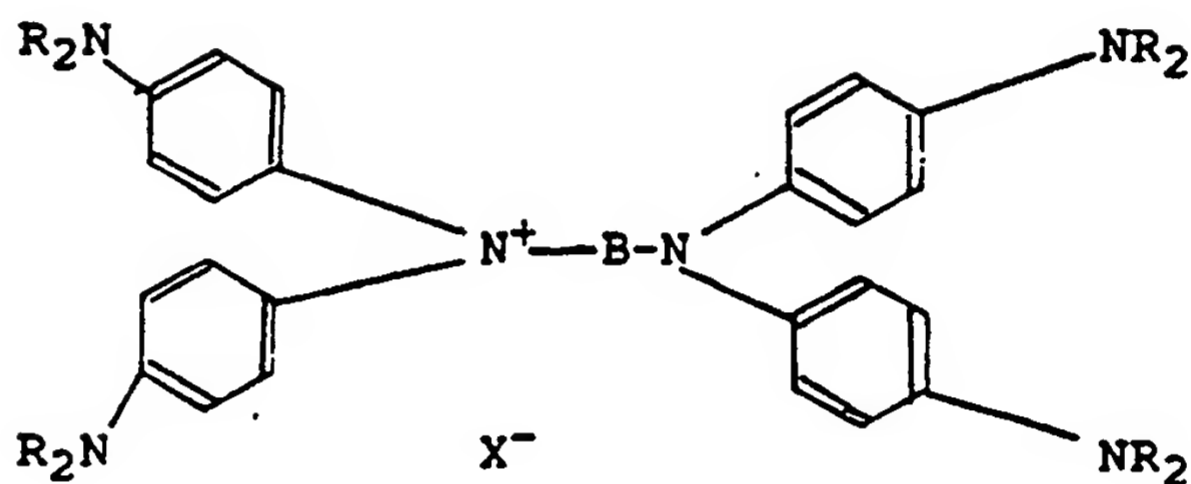
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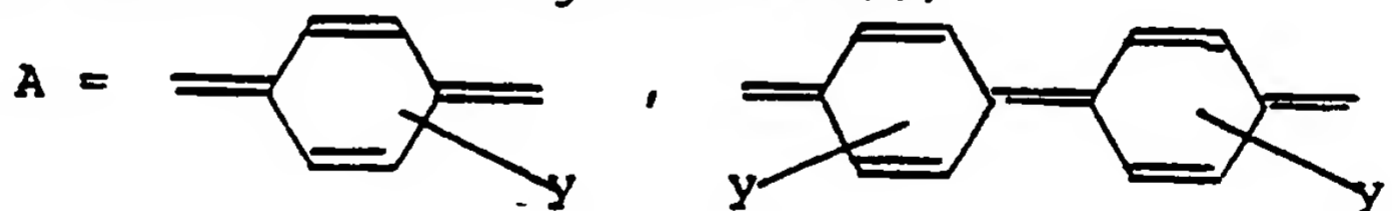
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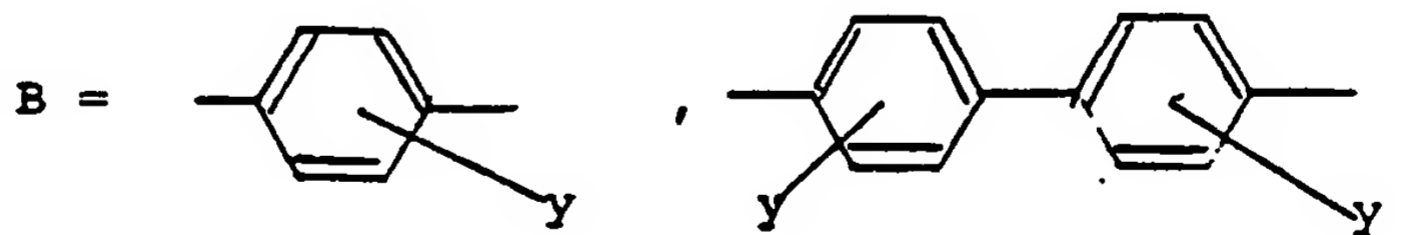
where  $R = \text{alkyl, benzyl, substituted benzyl etc.}$

$X = \text{SbF}_6^-, \text{BF}_4^-, \text{PF}_6^-, \text{AsF}_6^-, \text{ClO}_4^-, \text{B(phenyl)}_4, \text{triflate and other salts of strong acids which are not capable of electron donation to the cation radical or dication radical in the ground state;}$

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$Y = \text{hydrogen, alkyl, aryl, nitro, halo, benzyl, substituted benzyl, etc.}$

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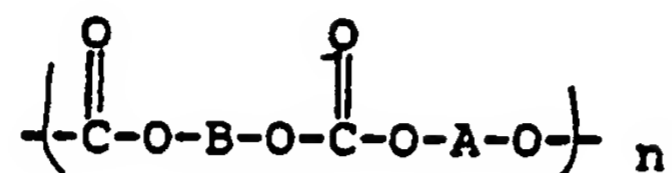
Examples of these sensitizers include the series of near infrared absorbers which go by the trade name Cyasorb IR 165, 126 and 99 from American Cyanamid as well as those IR absorbers described in U.S. Patent 4,656,121 which is incorporated herein by reference.

Furthermore, in general other sensitizers which can be employed include any cation radical and dication radical salts of strong acids which absorb strongly at the desired laser output wavelength. While an output wavelength of 1064 nm is preferred in certain color imaging and proofing applications, any wavelength can be employed where sufficient power is present to be effective for the desired application. The decomposable binders according to the present invention are those polymeric materials which undergo rapid acid catalyzed decomposition, preferably at temperatures less than about 200°C, and most preferably at temperatures less than about 100°C.

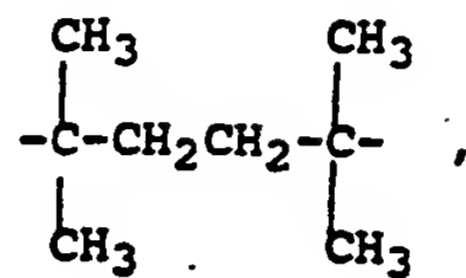
In particular, decomposable binders for use in this invention are those binders which decompose rapidly to give significant amounts of gases and volatile fragments at temperatures less than about 200°C and undergo significant reduction of decomposition temperature in the presence of small amounts of acids. Most desirable is the lowering of the decomposition temperature to less than about 100°C.

Examples of such polymers are nitrocellulose, polycarbonates, and materials of the type described in J.M.J. Frechet, F. Bouchard, F.M. Houlihan, B. Kryczke, E. Eichler, J. Imaging Science; 30(2) 59-64 (1986), and related materials which are described in detail in the balance of this disclosure.

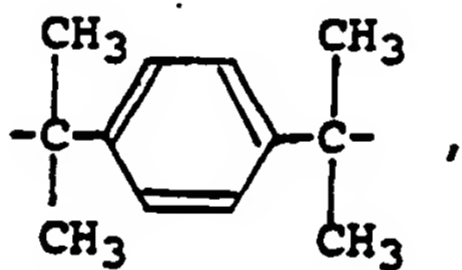
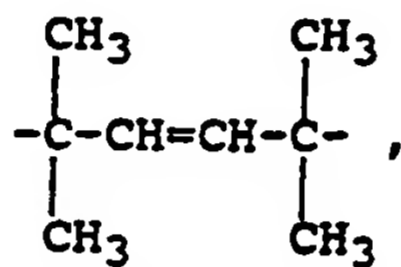
Examples of binders include polycarbonates having the structure:



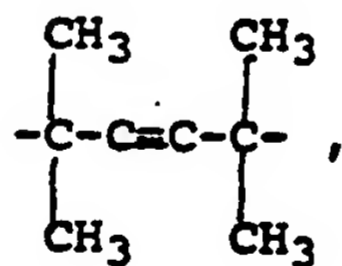
5 where B comprises



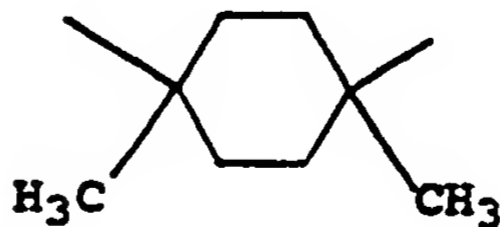
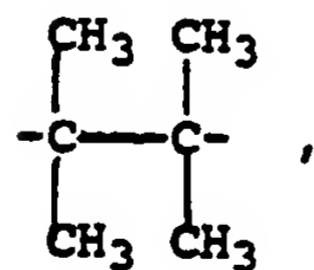
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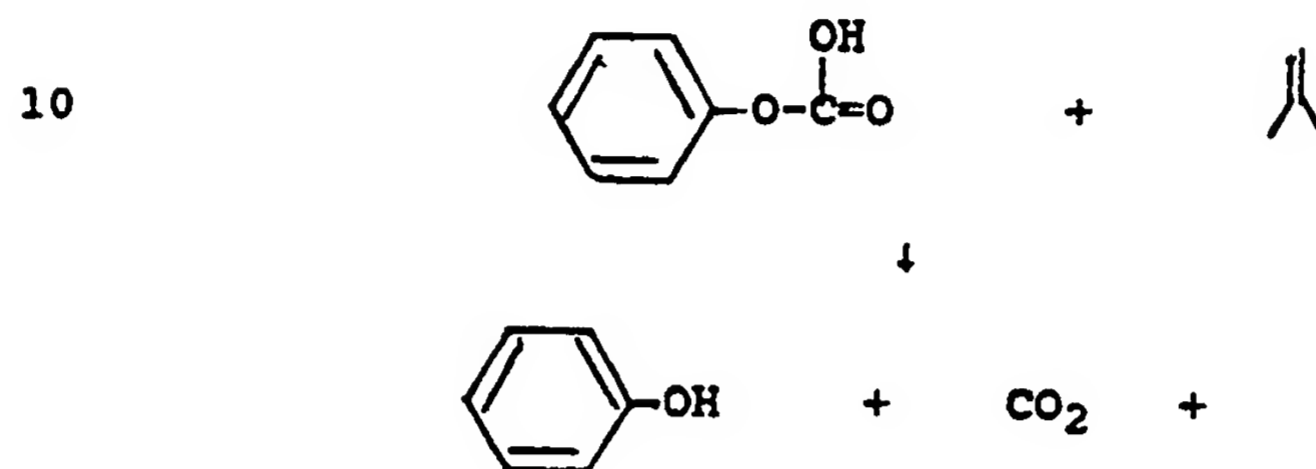
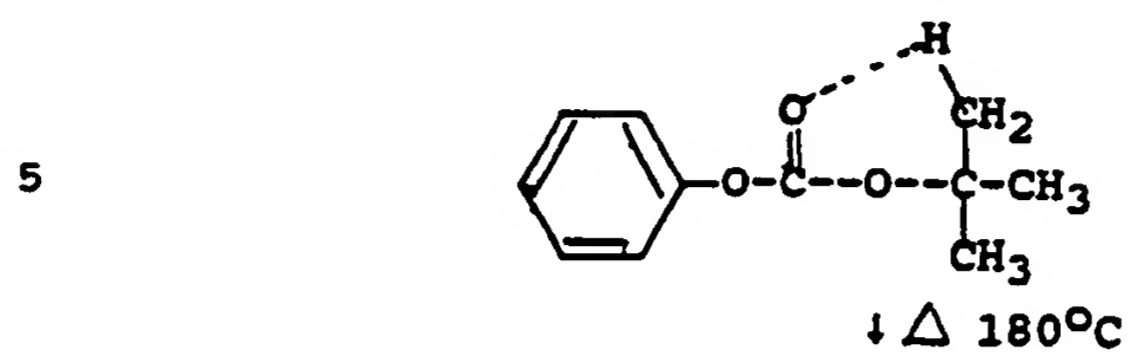
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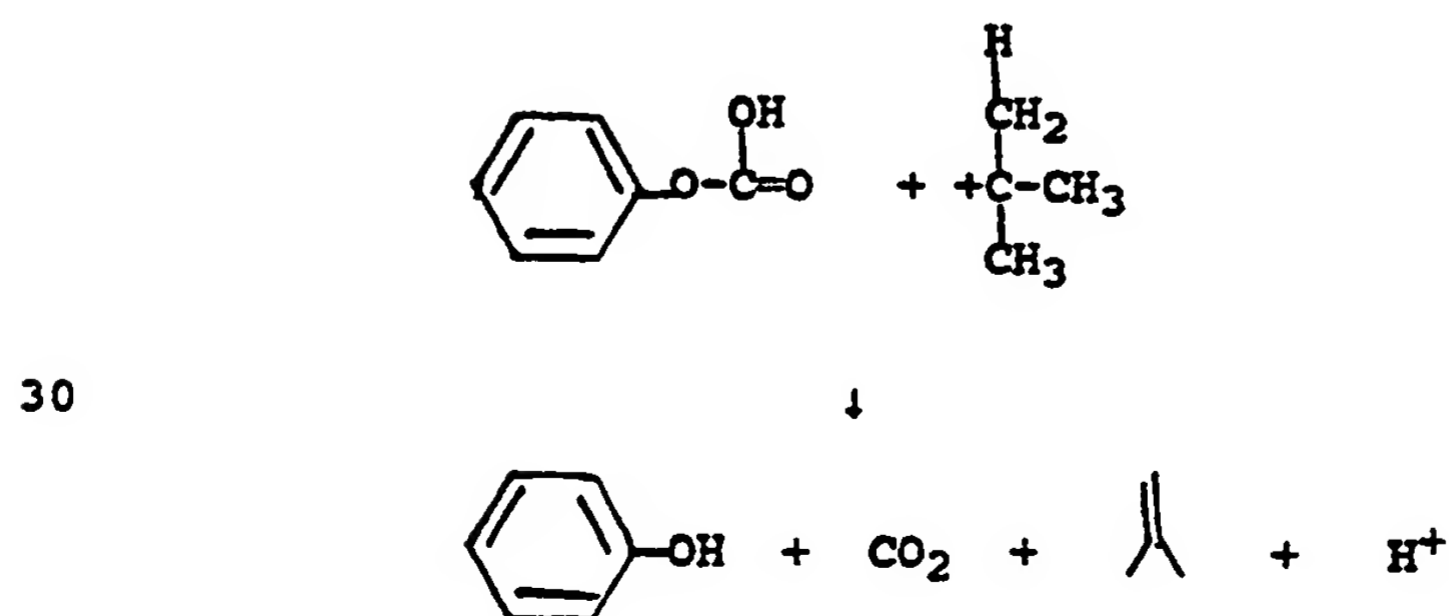
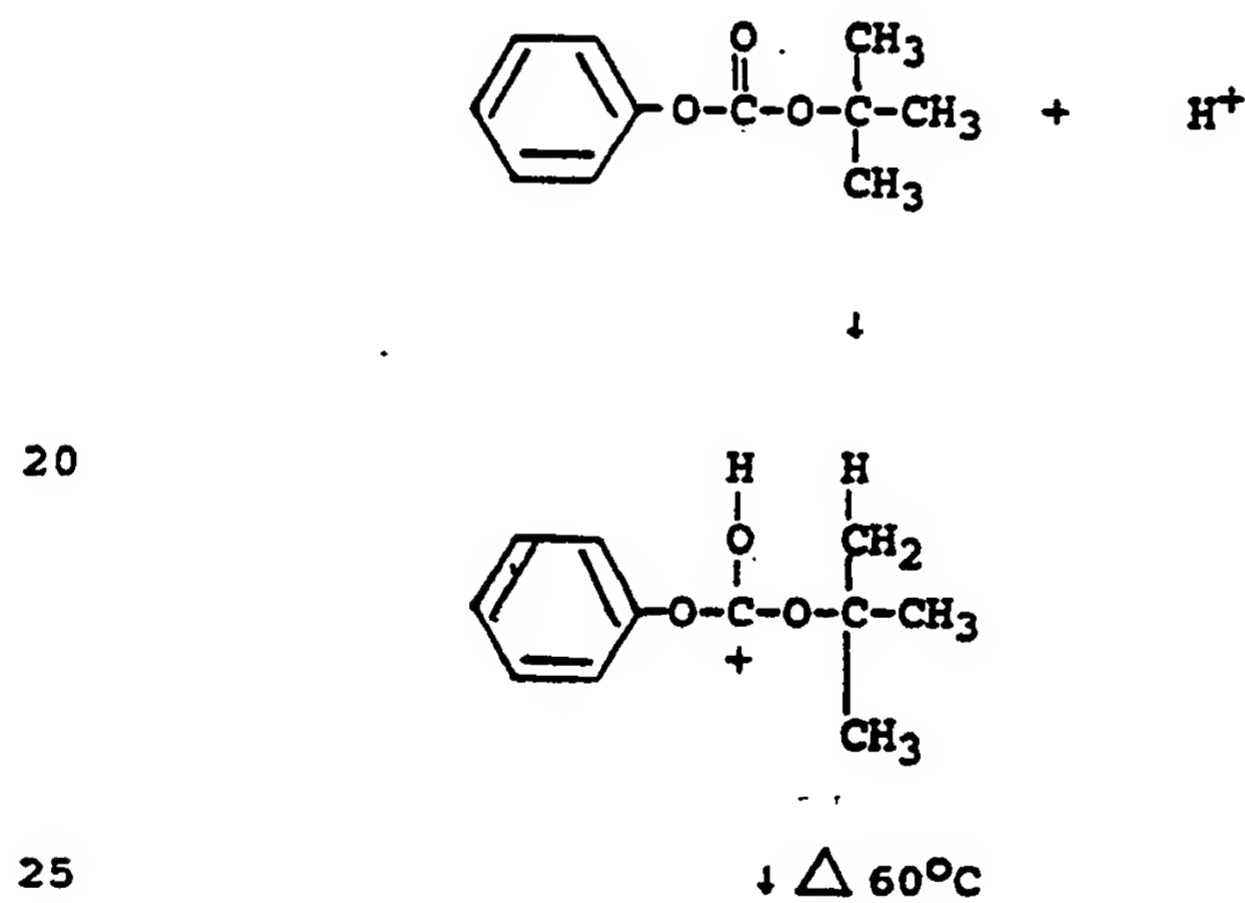
or other groups capable of generating a tertiary carbonium ion upon thermolysis and of producing gain or amplification in the decomposition of the polymer by eliminating a proton from the carbonium ion.

In other words, in addition to a thermal decomposition, as illustrated in the model system below:



the present invention preferably employs an acid catalyzed thermal decomposition,

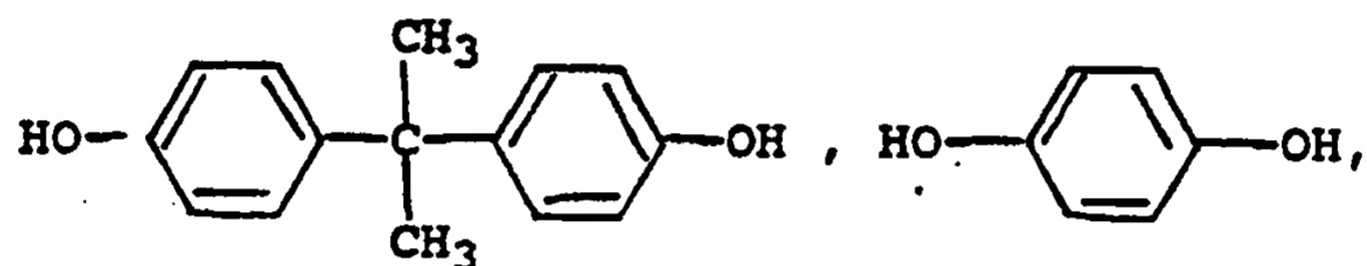
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as generally described by JMJ Frechet, et al, Journal of Imaging Science, 30(2)59(1986). Commercially available Bisphenol A polycarbonate decomposes at temperatures greater than 300°C. Non tertiary diols and polyols may be  
 5 polymerized in combination with tertiary diols to improve the physical properties of the polymer.

A may be the same as B or chosen from those dihydroxy aromatic or poly hydroxy compounds capable of polymerization to a polycarbonate.

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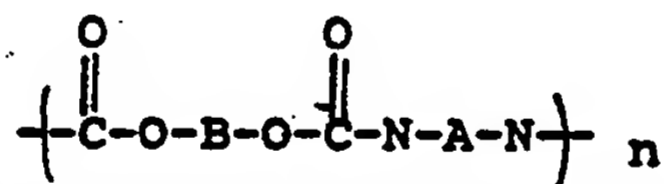


are preferred.

The synthesis of these polymers has been described, for example, by JMJ Frechet et al, Polymer Journal, 19(1),  
 15 pp. 31-49, (1987).

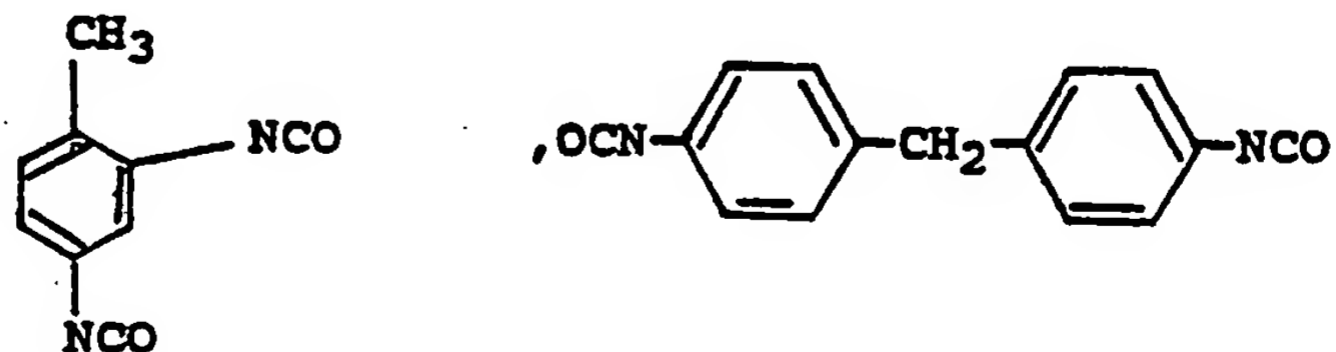
In addition to the polycarbonates, polyurethanes of the following general structure can also be employed:

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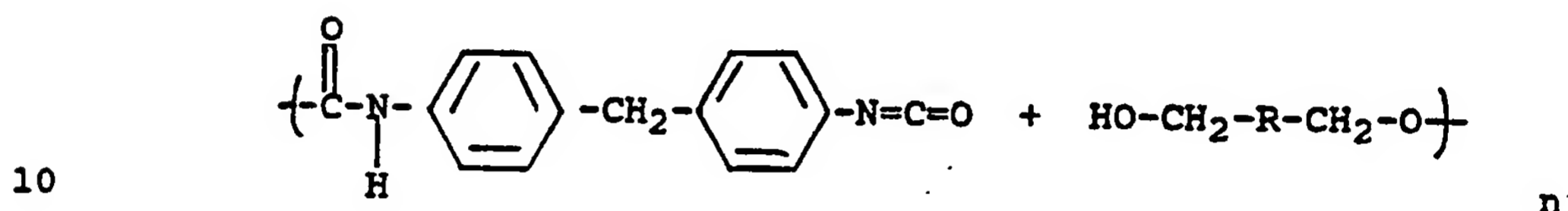
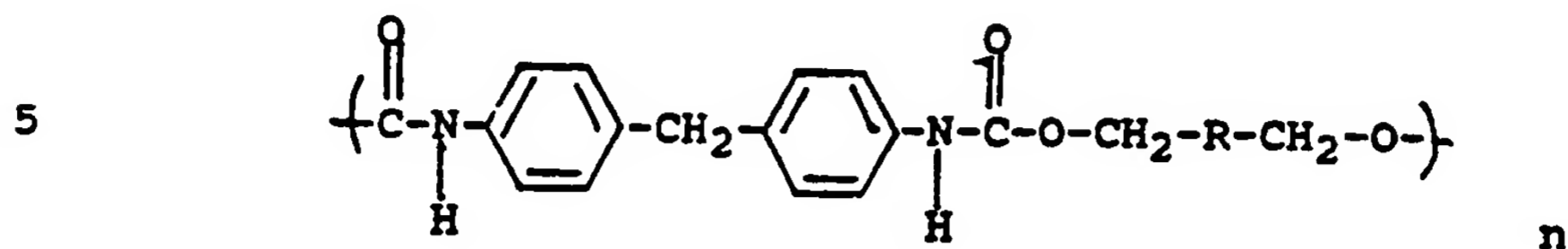
where B is as described above and A is chosen from those aromatic or aliphatic diisocyanate or polyisocyanates capable of copolymerization with the above tertiary diols to give a polyurethane.

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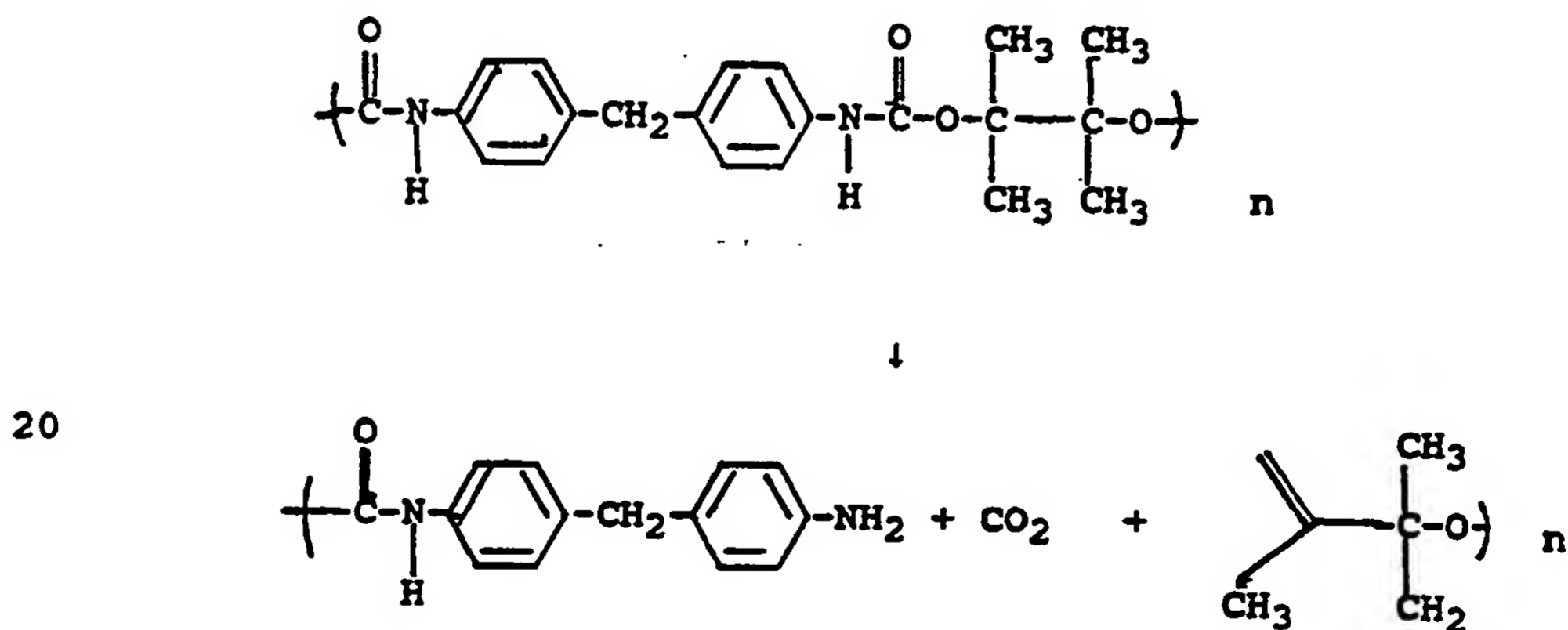
are preferred.

It is known that polyurethanes of primary and secondary diols and polyols decompose at temperatures greater than about 200°C:



where R is alkyl.

However, polyurethanes containing certain tertiary alcohol structural units can decompose at less than about 200°C by cleavage in a mechanism analogous to that of Frechet's polycarbonates as illustrated below:



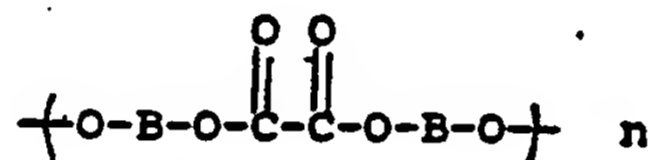
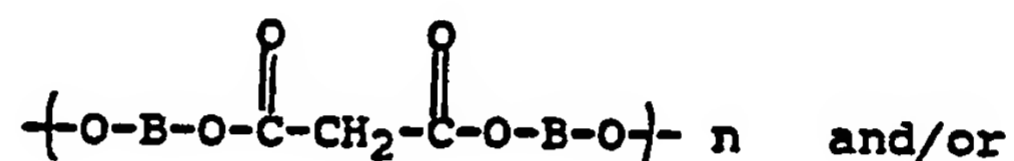
Similar to the case with polycarbonates illustrated

previously, the present invention preferably employs an acid catalyzed thermal decomposition with polyurethanes.

Small amounts (less than about 10%) of non-tertiary diols and polyols may be polymerized in combination with the  
5 tertiary diols to improve the physical properties of polymer.

The synthesis of these polyurethanes is shown within Example 1, *infra*.

In addition to polycarbonates, and polyurethanes, polyesters of the following general structure may be  
10 employed:



15 where B is described above. Polyorthoesters and polyacetals with analogous general structures may also be employed.

Small amounts (e.g., less than about 10%) of non-tertiary diols and polyols may be polymerized in combination with B to improve the physical properties of the polymer.

20 Small amounts (e.g., less than about 10%) of other compatible di- and polyacids may be polymerized in combination with malonic and oxalic acid to improve the physical properties of the polymer.

Alternating block copolymers containing polycarbonate, polyurethane, and/or polyester units as described  
25 above, as well as containing analogous polyorthoester and polyacetal units, may also be employed.

Examples of other polymers which are effective in the present invention include nitrocellulose with low  
30 viscosity, SS nitrocellulose being particularly preferred.

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Other examples of nitrocellulose which can be employed are described on pages 329-336 in Cellulose and Its Derivatives by Ister and Flegien which is incorporated herein by reference.

5           In addition, nitrocellulose can be added in the form of nitrocellulose containing printing inks which are compatible with the solvent used to dissolve the sensitizer. Examples of such compositions include solvent based gravure inks and process printing inks.

10          In addition, the nitrocellulose can be used alone or can be employed with other decomposable binders.

          As was previously discussed, the binder employed ideally is soluble within the same solvent which dissolves the near infrared absorbing sensitizer.  
15          However, dispersions may be used in appropriate circumstances when a mutual solvent cannot be found.

          The coating composition may also contain other materials which are non-absorbing at the desired laser emission wavelengths and/or non-decomposing and  
20          do not adversely affect the absorbance of the coating at the laser wavelength. These materials are chosen dependant upon the function of the final product to be produced. These materials may play a part in the imaging chemistry or may be inert.

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In a preferred embodiment, substances believed capable of donating H<sup>•</sup> (hydrogen atom) to the excited state of the sensitizer are included in the coating compositions, thereby increasing acid formation. Such materials include alcohols, thiols, phenols, amines, and hydrocarbons. Particularly preferred are low molecular weight secondary and tertiary alcohols, diols and polyols such as 1,2-decanediol, pinacol, 2,5-dimethylhexane-2,5 diol, 2,5-dimethyl-3-hexyne-2,5-diol and combinations of these. Addition of the hydrogen atom donors to the coating surprisingly enables the reduction of the amount of costly near IR absorber(s) from about 50% by weight based on solids to about 5 to about 15% by weight based on solids.

However, when nitrocellulose is employed as the polymeric binder, the use of an additional hydrogen atom donor material is not required because the desired hydrogen donors are already present within the resin. Such additional material may be nonetheless added if desired.

Examples of additions which also may be included are chosen dependent on the functions of the final product to be produced. The combined use of at least one hydrogen atom donating material and at least

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one additive is particularly preferred within the present invention.

When employing a laser having an output at 1064 nm wavelength, these additives can include visible  
5 or UV absorbing materials particularly those commonly used in the printing industry such as C.I. Blue 15, C.I. Yellow 17, C.I. Magenta 57, C.I. Black 7 or actual solvent based printing inks such as those available from American Inks and Coatings Co., plasticizers,  
10 surfactants, adhesion promoters and the like. Particularly preferred are dyes such as Morfast Brown 100, Morfast Violet 1001, Morfast Blue 105, Morfast Yellow 101, and Morfast Red 104 due to their high tinctorial strength (Morfast is a trademark of Morton  
15 Thiokol for a series of liquid dyes). In addition, when nitrocellulose is employed as the binder, the previously discussed nitrocellulose containing printing inks are preferred.

In terms of the coating, the sensitizer and  
20 decomposable binder are present in amounts sufficient to allow rapid partial decomposition of the binder to gaseous and non-gaseous products when the sensitizer interacts with laser light. Preferably, the decomposable binder is present in an amount of about 50  
25 to about 95% by weight of dry solids while the

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sensitizer is present in an amount of about 5 to about 50% by weight of dry solids. In addition, the additives can be present in an amount of about 0.5 to about 50% by weight of dry solids while the hydrogen atom donor can be present in an amount of about 1 to about 10% by weight of dry solids.

In producing the coating composition according to the present invention, a solution or dispersion is made which contains solvent, the near infrared absorbing sensitizer, the decomposable binder and, optionally, the hydrogen atom donor and/or additives. Preferably, the components of the wet coating are present in amounts of about 0.2 to about 5% by weight of the absorbing sensitizer, about 0.5 to about 20% by weight of the decomposable binder and, optionally, about 0.5 to about 2% by weight of a hydrogen atom donor and/or about 2 to about 20% by weight of the additives, with the remainder being solvent.

The solvent employed in the present invention includes those solvents which dissolve both the binders and preferably the near IR sensitizers. Examples of such solvents include chlorinated hydrocarbons, such as methylene chloride, 1,1,1-trichlorethane, chloroform, carbon tetrachloride, trichloromethane and the like;

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ketones such as acetone, methyl ethylketone, methyl propylketone and higher boiling analogues whose boiling points do not exceed the thermal decomposition thresholds of the binder resin, or mixtures thereof.

5           After the solution or dispersion is made, it is coated onto the support film by methods which are well-known in the art such as Meyer rod coating, gravure coating, reverse roll coating or extrusion coating. Because they are well known in the art, they  
10       are not further explained here.

          The support films employed can be either near infrared transparent support films or near infrared non-transparent support films. Transparent support films which can be employed by the present invention  
15       include polyesters, polycarbonates and any base which does not dissolve in the coating solvents employed, with polyesters being preferred. Examples of non-transparent support includes any non-transparent base which would not dissolve in the coating solvents  
20       employed. These supports can include aluminum supports, such as used in printing plates, glass substrates, and silicon chips.

          The coating is preferably employed in the amount of about 0.1 to about 0.5 grams dry wt/ft<sup>2</sup> and  
25       absorbance at 1064 nm of not less than 0.125.

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When the sensitizer is chosen so as to be substantially non-absorbing in the visible region (400-760 nm), the laser imaging materials of the present invention can be advantageously employed in a color  
5 imaging and proofing method. By this method, a receptor sheet is positioned and firmly held as in a vacuum frame relative to the above described laser imaging material in such a manner that it is effective in receiving materials which have been ablated from  
10 the surface of the imaging material.

Figure 1 illustrates the use of near infrared transparent supports in the method of the present invention. In this embodiment, laser beam, 4, contacts the material which comprises the laser transparent  
15 support, 1, the laser abatable coating, 2, and the receiver sheet, 3, on the back or support side of the material.

Figure 2 illustrates an alternative embodiment of the present invention wherein the material uses a near infrared nontransparent support 5.  
20 In this embodiment the receiver sheet, 3, is made of near infrared transparent material and the laser beam contacts the material on the front or receiver sheet side of the material.

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In either embodiment, laser radiation, at the desired wavelength is introduced onto the absorbing layer so as to cause rapid partial decomposition of the binder(s) to gaseous products. The rapid expansion of the heated gases causes ablation of the coating layer to the receptor sheet thus producing an imaged color film or intermediate master, 6, (i.e., the laser donor imaging material) and a color print or proof, 7, (i.e., the receptor sheet).

The receptor sheet employed can include those which are well-known in the art of proofing such as newsprint, coated or uncoated papers of all shades and color, opaque filled, and opaque coated plastic sheets with the printing stock to be employed in the particular color proofing application being preferred. It can also include those which are known in the art of color hard copy printing such as transparent and opaque films and various coated and uncoated papers.

Moreover, because the decomposable binder and sensitizer are transparent in the visible range, materials such as UV, visible and near IR absorbing dyes and/or pigments can be added to the coating. This also allows the material to be used in applications such as color printing and proofing, which prior ablative materials simply could not address.

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In order to further illustrate the present invention and the advantages associated therewith, the following specific examples are given, it being understood that same are intended only as illustrative and in nowise limitative.

EXAMPLE 1

Polyurethane Synthesis (Polymer VII from Table 1):

2,4-Toluene diisocyanate (TDI), 20g, 2,5-dimethyl-3-hexyne-2,5-diol, 16.3 g., dibutyltin dilaurate, 5 drops and N-methyl pyrrolidone, 50 ml, were added to a 200 ml flask equipped with magnetic stir bar and nitrogen inlet. The solution was stirred 6 hours at 50°C, then at room temperature overnight. The polymer was isolated by precipitation from water. Polymers gave MW  $\approx$  7,000 by GPC with thermal decomposition at 165°C by DSC (scan rate of 25°C/min).

TABLE 1

The following polyurethanes were synthesized according to the general procedure in Example 1 and the following polycarbonates were synthesized as described in J.M.J. Frechet, et al, Polymer Journal, 19(1), pp. 31-49, (1987):

10				
15		V	VI	III
20		VII	VIII	IV
25		IX	X	
		XI	XII	

The above polymers were evaluated by DSC.

The following results were obtained:

TABLE 2

5	<u>POLYMER</u>	<u>SOFT/MELT</u>	<u>MELT ENERGY</u>	<u>DECOMPOSITION</u>
		<u>TEMP. (°C)</u>	<u>(J/g)</u>	<u>TEMP. (°C)</u>
	III	139	22	180
	IV	50	21	170
	V	-	-	200
	VI	-	-	110
10	VII	46	85	165
	VIII	100	-	113
	IX	-	-	157
	X	63	-	100
	XI	94	22	206
15	XII	50	100	174
	Ethyl cellulose	96	17	203
	Polyacetal	-	-	171

EXAMPLE 2

The following solution was made and coated on  
polyester film with #4 Meyer rod at a loading of 0.5g wet  
weight/ft<sup>2</sup>. Addition of components was in the order indi-  
cated:

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	7.25g	Acetone
	1.197g	Copolymer of 2,4 TDI & 2,5-dimethyl-3-hexyne-2,5-diol (Polymer VII from Table 1)
5	0.364g	Cyasorb IR 165
	0.12g	2,5-Dimethyl-3-hexyne-2,5-diol
	1.06g	Morfast Yellow 101

10 The yellow film was imaged using a yellow separation film master on the Crosfield Datrax 765 at 9.8 W ( $0.16\text{J}/\text{cm}^2$ ) to give an imaged yellow film and a reversal yellow print on a newsprint receptor sheet. The Datrax 765 is commercial laser imaging hardware from Crosfield Electronics, Ltd. which employs a 1064 nm Nd:YAG laser with 5-15W of available power:

### EXAMPLE 3

15 The above solution was made substituting a combination of 0.76g Morfast Red 104 and 0.04 g Morfast Brown Violet 1001 in place of Morfast Yellow in Example 2. The films were imaged using a magenta separation film master as above with the yellow print on newsprint from Example 2 used as receptor  
20 sheet to produce a two color print along with an imaged magenta film.

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EXAMPLE 4

The above solution was made substituting a combination of 0.4g Morfast Blue 105 and 0.4g Morfast Brown 100 in place of Morfast Yellow in Example 2. The films were imaged onto the above two color print receptor sheet from Example 3 using a cyan film master to give a three color print along with an imaged cyan film.

EXAMPLE 5

The above solution was made substituting a combination of Morfast Brown 100 and Morfast Blue 105 and Morfast Red 104 (total weight of 1.06g in place of Morfast Yellow in Example 2) color balanced to give a neutral black film. The films were imaged using a black separation master onto the three color print receptor sheet from Example 4 to give a full color print suitable for color proofing along with an imaged neutral black film.

EXAMPLE 6

The following solution was made and coated as described in Examples 2 through 5.

20	7.25 g	Acetone
	0.364g	Cyasorb IR 165
	2.5g	American Ink & Coatings Co. gravure inks

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Process Yellow orProcess Red orProcess Blue or

Process Black.

5           The American Ink gravure inks include  
nitrocellulose which is the decomposable binder. Films are  
imaged as described in Examples 2 through 5 to give full  
color prints along with individual imaged monocolor and black  
films.

10

EXAMPLE 7

The following solution is made and coated as  
described in Examples 2 through 5.

	7.25 g	Acetone
	1.197 g	Copolymer of 4,4'diphenyl methane
15		diisocyanate and PARADIOL (trade
		name of Goodyear Chemicals)
		(Polymer X from Table 1)
	0.364g	Cyasorb IR 165
	0.12g	2,5-Dimethyl-3-hexyne-2,5-diol
20	2.5g	American Ink & Coatings Co.
		gravure inks
		Process Yellow <u>or</u>
		Process Red <u>or</u>
		Process Blue <u>or</u>
25		Process Black.

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Films are imaged as described in Examples 2 through 5 to give full color prints along with individual imaged monicolor and black films.

#### EXAMPLE 8

5                   To 8.35g of a 50:50 mixture of 1,1,1-trichloro-ethane and methylene chloride is added 0.5g of an alternating polycarbonate synthesized from Bisphenol A and 2,5-dimethyl hexane-2,5-diol (Polymer III from Table 1); 0.1g Cyasorb IR 165; 0.1g 2,5-dimethyl-3-hexyne-2,5-diol; and 1.0g of any of  
10   the Morfast colors described above. The solution was coated at a loading of 1g of solution/sq.ft. with a #9 Meyer rod by hand drawdown. The dried films are imaged at  $0.11 \text{ J/cm}^2$  on a Crosfield Datrax 765 to give a color print on a receptor sheet and imaged monicolor or black films. The thickness of  
15   the dry coating can be adjusted to vary the optical density to a desired level. Optical density differences between the imaged and unimaged areas ranging from 0.5 to 2.0 are typically achieved for the imaged films (transmission density) and for the receptor sheets (reflectance density)  
20   when measured using the appropriate color filters on the densitometers.

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EXAMPLE 9

To 9.35g of a 50:50 mixture of 1,1,1-trichloroethane and methylene chloride was added 0.5g of an alternating polycarbonate from Bisphenol A and 2,5-dimethyl-3-hexyne-2,5-diol (Polymer IV from Table 1); 0.1g Cyasorb IR 165; and 0.05g of 2,5-dimethyl-3-hexyne-2,5-diol. The solution was coated on polyester film and imaged at 0.08 J/cm<sup>2</sup> as described above to give an imaged light tan film and a reversal light tan image on a newsprint receptor sheet.

By comparison films using bisphenol A polycarbonates, polyvinylidene chloride (Saran F120 or F300), polymethacrylonitrile, ethylcellulose N-7, or styrene/acrylonitrile copolymer as binders in the place of decomposable polycarbonate or polyurethanes gave very little or no image transfer to the receptor sheet.

While this invention has been described in terms of various preferred embodiments, the skilled artisan will appreciate that various modifications, substitutions, omissions and changes may be made without departing from the spirit thereof. Accordingly, it is intended that the scope of the present invention be limited solely by the scope of the following claims including equivalents thereof.

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CLAIMS

1. A near infrared absorbing coating composition which can be useful in color imaging and proofing comprising a solution or dispersion containing  
5 (a) at least one sensitizer which absorbs light at a desired infrared wavelength for a particular laser output, and (b) at least one decomposable binder wherein the at least one sensitizer is present in an amount which is effective to allow the rapid partial  
10 decomposition of the at least one binder when the coating is coated onto a support and the at least one sensitizer interacts with laser light.
2. The near infrared absorbing coating composition of claim 1, wherein the solution or  
15 dispersion further contains (c) at least one material which is nonabsorbing at the desired infrared wavelength and/or nondecomposing.
3. The near infrared absorbing coating composition of claim 2 wherein (c) comprises at least  
20 one material capable of donating hydrogen atoms to a photo excited state of the sensitizer.

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4. The near infrared absorbing coating composition of claim 1 wherein at least one sensitizer is capable of initiating acid formation.

5 5. The near infrared absorbing coating composition of claim 4 wherein the at least one sensitizer is substantially non-absorbing in the visible region.

10 6. The near infrared absorbing coating composition of claim 1, wherein the at least one sensitizer comprises a dication radical or cation radical salt of a strong acid.

15 7. The near infrared absorbing coating composition of claim 3, wherein the at least one sensitizer comprises a dication radical or cation radical salt of a strong acid.

20 8. The near infrared absorbing coating composition of claim 1, wherein the at least one decomposable binder comprises a polymeric material capable of undergoing rapid acid catalyzed decomposition.

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9. The near infrared absorbing coating composition of claim 3, wherein the at least one decomposable binder comprises a polymeric material capable of undergoing rapid acid catalyzed decomposition.

10. The near infrared absorbing coating composition of claim 1 wherein the at least one decomposable binder undergoes decomposition at a temperature less than about 200°C.

11. The near infrared absorbing coating composition of claim 3 wherein the at least one decomposable binder undergoes decomposition at a temperature less than 200°C.

12. The near infrared absorbing coating composition of claim 1, wherein said at least one decomposable binder comprises nitrocellulose, a polycarbonate, a polyurethane, a polyester, a polyorthoester, a polyacetal, alternating and block copolymers containing decomposable polycarbonate, polyester, polyorthoester, polyacetal, and/or polyurethane units, or mixtures thereof.

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13. The laser absorbing coating composition of claim 3, wherein said at least one decomposable binder comprises nitrocellulose, a polycarbonate, a polyurethane, a polyester, a polyorthoester, a polyacetal, alternating and block copolymers containing decomposable polycarbonate, polyester, polyorthoester, polyacetal, and/or polyurethane units, or mixtures thereof.

14. The near infrared absorbing coating composition of claim 11, wherein the binder comprises nitrocellulose which comprises SS nitrocellulose, a solvent based gravure ink, a process printing ink, or mixtures thereof.

15. The near infrared absorbing coating composition of claim 3 where said hydrogen atom donating material comprises a low molecular weight secondary or tertiary alcohol, diol or polyol or mixtures thereof.

16. The near infrared absorbing coating composition of claim 3 where said hydrogen atom

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donating material is present in an amount of about 1 to about 10% by weight based on dry coating.

17. The near infrared absorbing coating composition of claim 2 wherein (c) comprises at least one additive.

18. The near infrared absorbing coating composition of claim 3 wherein (c) further comprises at least one additive.

19. The near infrared absorbing coating composition according to claim 17, wherein the additive comprises visible absorbing materials, UV absorbing materials, near IR absorbing materials, printing inks, plasticizers, surfactants, adhesion promoters, dispersing aids, or mixtures thereof.

20. The near infrared absorbing coating composition of claim 17, wherein the additive is present in an amount of about 0.5 to about 50% by weight of dry coating.

21. The near infrared absorbing coating composition of claim 1, wherein the at least one

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sensitizer is present in the amount of about 5 to about 50% by weight of dry coating.

22. The near infrared absorbing coating composition of claim 3, wherein the at least one  
5 sensitizer is present in the amount of about 5 to about 50% by weight of dry coating.

23. The near infrared absorbing coating composition of claim 1, wherein said decomposable  
binder is present in an amount of about 50 to about 95%  
10 by weight of dry coating.

24. The near infrared absorbing coating composition of claim 3, wherein said decomposable  
binder is present in an amount of about 50 to about 95%  
by weight of dry coating.

15 25. The near infrared absorbing coating composition of claim 1, wherein the solvent comprises a chlorinated hydrocarbon, a ketone or mixtures thereof.

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26. The near infrared absorbing coating composition of claim 3, wherein the solvent comprises a chlorinated hydrocarbon, a ketone or mixtures thereof.

27. A laser imaging material which can be  
5 useful in color printing and proofing comprising a support film having a near infrared laser absorbing layer thereon wherein said layer comprises (a) at least one sensitizer which absorbs light at a desired  
infrared wavelength for a particular laser output, and  
10 (b) at least one decomposable binder wherein the at least one sensitizer is present in an amount effective to allow the rapid partial decomposition of the at least one binder when the at least one sensitizer interacts with laser light.

15 28. The laser imaging material of claim 27, wherein the layer further comprises (c) at least one material which is nonabsorbing at the desired near infrared wavelength and/or nondecomposing.

29. The laser imaging material of claim 28  
20 where (c) comprises at least one material capable of donating a hydrogen atom to a photo excited state of the sensitizer.

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30. The laser imaging material of claim 27 wherein at least one sensitizer is capable of initiating acid formation.

5 31. The laser imaging material of claim 27, wherein the at least one sensitizer is substantially non-absorbing in the visible range.

32. The laser imaging material of claim 27, wherein at least one sensitizer comprises a cation  
10 radical or dication radical salt of a strong acid.

33. The laser imaging material of claim 29, wherein at least one sensitizer comprises a cation radical or dication radical salt of a strong acid.

34. The laser imaging material of claim 27,  
15 wherein the at least one decomposable binder comprises a polymeric material capable of undergoing rapid acid catalyzed decomposition.

35. The laser imaging material of claim 29, wherein the at least one decomposable binder comprises

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a polymeric material capable of undergoing rapid acid catalyzed decomposition.

36. The laser imaging material of claim 27 wherein the at least one decomposable binder undergoes decomposition at a temperature less than about 200°C.

37. The laser imaging material of claim 29 wherein the at least one decomposable binder undergoes decomposition at a temperature less than about 200°C.

38. The laser imaging material of claim 27, wherein said at least one decomposable binder comprises nitrocellulose, a polycarbonate, a polyurethane, a polyester, a polyorthoester, a polyacetal, alternating and block copolymers containing decomposable polycarbonate, polyester, polyorthoester, polyacetal and/or polyurethane units, or mixtures thereof.

39. The laser imaging material of claim 29, wherein said at least one decomposable binder comprises nitrocellulose, a polycarbonate, a polyurethane, a polyester, a polyorthoester, a polyacetal, alternating and block copolymers containing decomposable

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polycarbonate, polyester, polyorthoester, polyacetal and/or polyurethane units, or mixtures thereof.

40. The laser imaging material of claim 37, wherein the binder comprises nitrocellulose which  
5 comprises SS nitrocellulose, a solvent based gravure ink, a printing process ink, or mixtures thereof.

41. The laser imaging material of claim 37 wherein the decomposable binder further comprises an additional polymeric material which undergoes acid  
10 catalyzed decomposition at temperatures less than about 200°C.

42. The laser imaging material of claim 27 wherein the support film comprises a near infrared transparent support film.  
15

43. The laser imaging material of claim 42 wherein the support film comprises a polyester or a polycarbonate.

44. The laser imaging material of claim 27  
20 wherein the support film comprises a near infrared non-transparent support film.

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45. The laser imaging material of claim 29 where said hydrogen atom donating material comprises a low molecular weight secondary or tertiary alcohol, diol or polyol or mixtures thereof.

5           46. The laser imaging material of claim 29 where said hydrogen atom donating material is present in an amount of 1 to about 10% by weight based on dry coating.

10           47. The laser imaging material of claim 28 wherein (c) comprises at least one additive.

48. The laser imaging material of claim 29 wherein (c) further comprises at least one additive.

15           49. The laser imaging material of claim 47, wherein the at least one additive comprises visible absorbing materials, UV absorbing materials, near IR absorbing materials, printing inks, dispersing aids, plasticizer, surfactants, adhesion promoters or mixtures thereof.

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50. The laser imaging material of claim 49, wherein the at least one additive is present in an amount of about 0.5 to about 50% by weight of dry coating.

5 51. The laser imaging material of claim 27, wherein the at least one sensitizer is present in an amount of about 5 to about 50% by weight of dry coating.

10 52. The laser imaging material of claim 27, wherein said decomposable binder is present in an amount of about 50 to about 95% by weight of dry coating.

53. A method for providing an imaged film and a color print or proof comprising:

15 providing a color imaging donor material which comprises a support film having a near infrared absorbing layer thereon wherein said layer comprises (a) at least one sensitizer which absorbs at a desired infrared wavelength for a particular laser output, (b)  
20 at least one decomposable binder and (c) at least one material which is nonabsorbing at the desired near infrared wavelength and/or nondecomposing wherein (a)

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is present in an amount effective to allow the rapid partial decomposition of the at least one decomposable binder when (a) interacts with laser light;

providing a receptor sheet positioned  
5 relative to the color imaging donor material in such a manner that it is effective in receiving material which has been ablated from the surface of the imaging donor material; and

introducing a laser output having the desired  
10 near infrared wavelength onto the surface of the color imaging donor material so as to cause ablation of material from the surface of the coating onto the receptor sheet thereby forming both an imaged donor film and a color print or proof of reversed sign on the  
15 receptor sheet.

54. The method of claim 53 wherein (c) comprises a material capable of donating a hydrogen atom to a photo excited state of the sensitizer.

55. The method of claim 53 wherein the at  
20 least one sensitizer is capable of initiating acid formation.

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56. The method of claim 53, wherein the at least one sensitizer is substantially non-absorbing in the visible range.

57. The method of claim 53, wherein the at least one sensitizer comprises a cation radical or dication radical salt of a strong acid.

58. The method of claim 53, wherein the at least one decomposable binder comprises a polymeric material capable of undergoing rapid acid catalyzed decomposition.

59. The method of claim 54, wherein the at least one decomposable binder comprises a polymeric material capable of undergoing rapid acid catalyzed decomposition.

60. The method of claim 53 wherein the at least one decomposable binder undergoes decomposition at a temperature less than about 200°C.

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61. The method of claim 54 wherein the at least one decomposable binder undergoes decomposition at a temperature less than about 200°C.

62. The method of claim 53, wherein said at least one decomposable binder comprises nitrocellulose, a polycarbonate, a polyurethane, a polyester, a polyorthoester, a polyacetal, alternating and block copolymers containing decomposable polycarbonate, polyester, polyorthoester, polyacetal and/or polyurethane units, or mixtures thereof.

63. The method of claim 54, wherein said at least one decomposable binder comprises nitrocellulose, a polycarbonate, a polyurethane, a polyester, a polyorthoester, a polyacetal, alternating and block copolymers containing decomposable polycarbonate, polyester, polyorthoester, polyacetal and/or polyurethane units, or mixtures thereof.

64. The method of claim 62, wherein the at least one decomposable binder comprises nitrocellulose which comprises SS nitrocellulose, a solvent based gravure ink, a printing process ink or mixtures thereof.

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65. The method of claim 54 where said hydrogen atom donating material comprises a low molecular weight secondary or tertiary alcohol, diol, polyol or mixtures thereof.

5           66. The method of claim 54 where said hydrogen atom donating material is present in an amount of about 1 to about 10% by weight based on dry solids.

67. The method of claim 53 wherein (c) comprises an additive.

10           68. The method of claim 54 wherein (c) further comprises an additive.

15           69. The method of claim 67, wherein the additive comprises visible absorbing dyes, UV absorbing dyes, near IR absorbing dyes, visible absorbing pigments, UV absorbing pigments, near IR absorbing pigments, plasticizers, surfactants, adhesion promoters, dispersing aids, printing inks or mixtures thereof.

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70. The method of claim 69, wherein the additive is present in an amount of about 0.5 to about 50% by weight.

5 71. The method of claim 53, wherein the at least one sensitizer is present in the amount of about 5 to about 50% by weight based on the dry solids.

10 72. The method of claim 53, wherein the at least one decomposable polymeric binder is present in an amount of 50 to 95% by weight based on the dry solids.

73. The method of claim 53 wherein the support film comprises a near infrared transparent support film.

15 74. The method of claim 73 wherein the near infrared transparent support film comprises a polyester or a polycarbonate.

75. The method of claim 53 wherein the support film comprises a near infrared non-transparent support film.

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76. The method of claim 53 wherein the near infrared absorbing layer is transparent to light in the visible range.

77. The method according to claim 54 wherein  
5 the at least one decomposable binder comprises at least one polymeric material capable of undergoing rapid acid catalyzed decomposition at a temperature of less than about 200°C, the at least one sensitizer comprises at least one cation radical or a dication radical salt of  
10 a strong acid, and said hydrogen atom donating material comprises a low molecular weight secondary or tertiary alcohol, diol, polyol or mixtures thereof.

78. The method according to claim 77 wherein  
the at least one sensitizer is present in the amount of  
15 about 5 to about 50% by weight of the dry coating, the at least one decomposable binder is present in an amount of about 50 to about 95% by weight of the dry coating, and hydrogen atom donating material is present  
in the amount of about 1 to about 10% by weight of the  
20 dry coating.

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79. The near infrared absorbing coating composition of claim 1 wherein the coating is transparent to light in the visible range.

80. The near infrared absorbing coating according to claim 3 wherein that at least one decomposable binder comprises at least one polymeric material capable of undergoing rapid acid catalyzed decomposition at a temperature of less than about 200°C, the at least one sensitizer comprises at least one cation radical or a dication radical salt of a strong acid, and said hydrogen atom donating material comprises a low molecular weight secondary or tertiary alcohol, diol, polyol or mixtures thereof.

81. The near infrared absorbing coating according to claim 80 wherein the at least one sensitizer is present in the amount of about 5 to about 50% by weight of the dry coating, the at least one decomposable binder is present in an amount of about 50 to about 95% by weight of the dry coating, and the hydrogen atom donating materials present in the amount of about 1 to about 10% by weight of the dry coating.

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82. The near infrared absorbing coating composition according to claim 18, wherein the additive comprises visible absorbing materials, UV absorbing materials, near IR absorbing materials, printing inks, plasticizers, surfactants, adhesion promoters, dispersing aids, or mixtures thereof.

83. The near infrared absorbing coating composition of claim 18, wherein the additive is present in an amount of about 0.5 to about 50% by weight of dry coating.

84. The laser imaging material of claim 27 wherein the near infrared laser absorbing layer is transparent to light in the visible range.

85. The laser imaging material according to claim 29 wherein the at least one decomposable binder comprises at least one polymeric material capable of undergoing rapid acid catalyzed decomposition at a temperature of less than about 200°C, the at least one sensitizer comprises at least one cation radical or a dication radical salt of a strong acid, and said hydrogen atom donating material comprises a low

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molecular weight secondary or tertiary alcohol, diol, polyol or mixtures thereof.

86. The laser imaging material according to claim 85 wherein the at least one sensitizer is present in the amount of about 5 to about 50% by weight of the dry coating, the at least one decomposable binder is present in an amount of about 50 to about 95% by weight of the dry coating, and said hydrogen atom donating materials present in the amount of about 1 to about 10% by weight of the dry coating.

87. A near infrared absorbing coating composition which can be useful in color imaging and proofing comprising a solution or dispersion containing a near infrared sensitive material and at least one decomposable binder, wherein the near infrared sensitive material consists essentially of at least one sensitizer which absorbs light at a desired infrared wavelength for a particular laser output.

88. A laser imaging material which can be useful in color printing and proofing comprising a support film having a near infrared laser absorbing layer there n wherein said layer c mprises a near

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infrared sensitive material and at least one  
decomposable binder wherein the near infrared  
sensitive material consists essentially of at least one  
sensitizer which absorbs light at a desired infrared  
5 wavelength for a particular laser output.

89. A method for providing an imaged film  
and a color print or proof comprising:

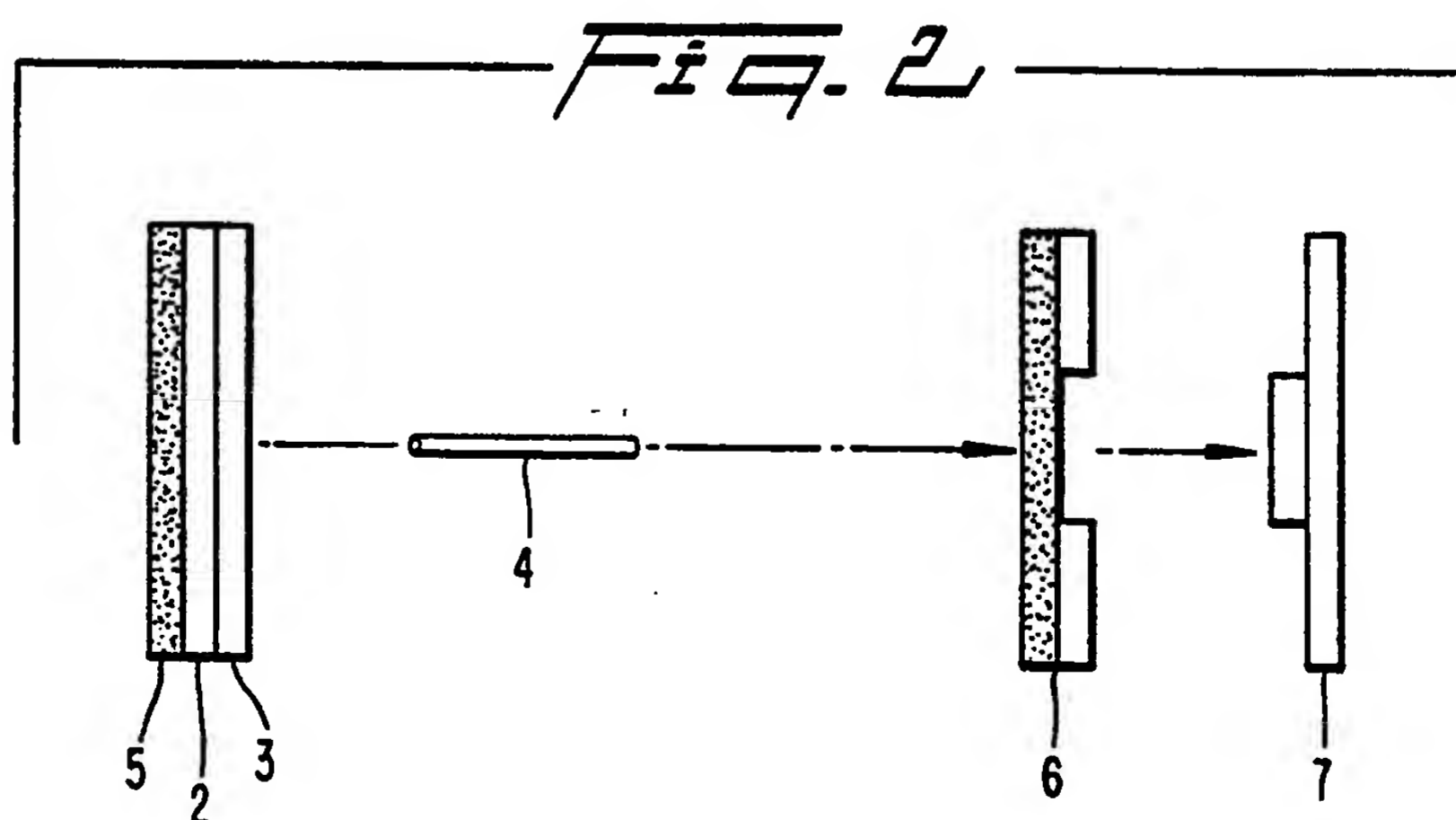
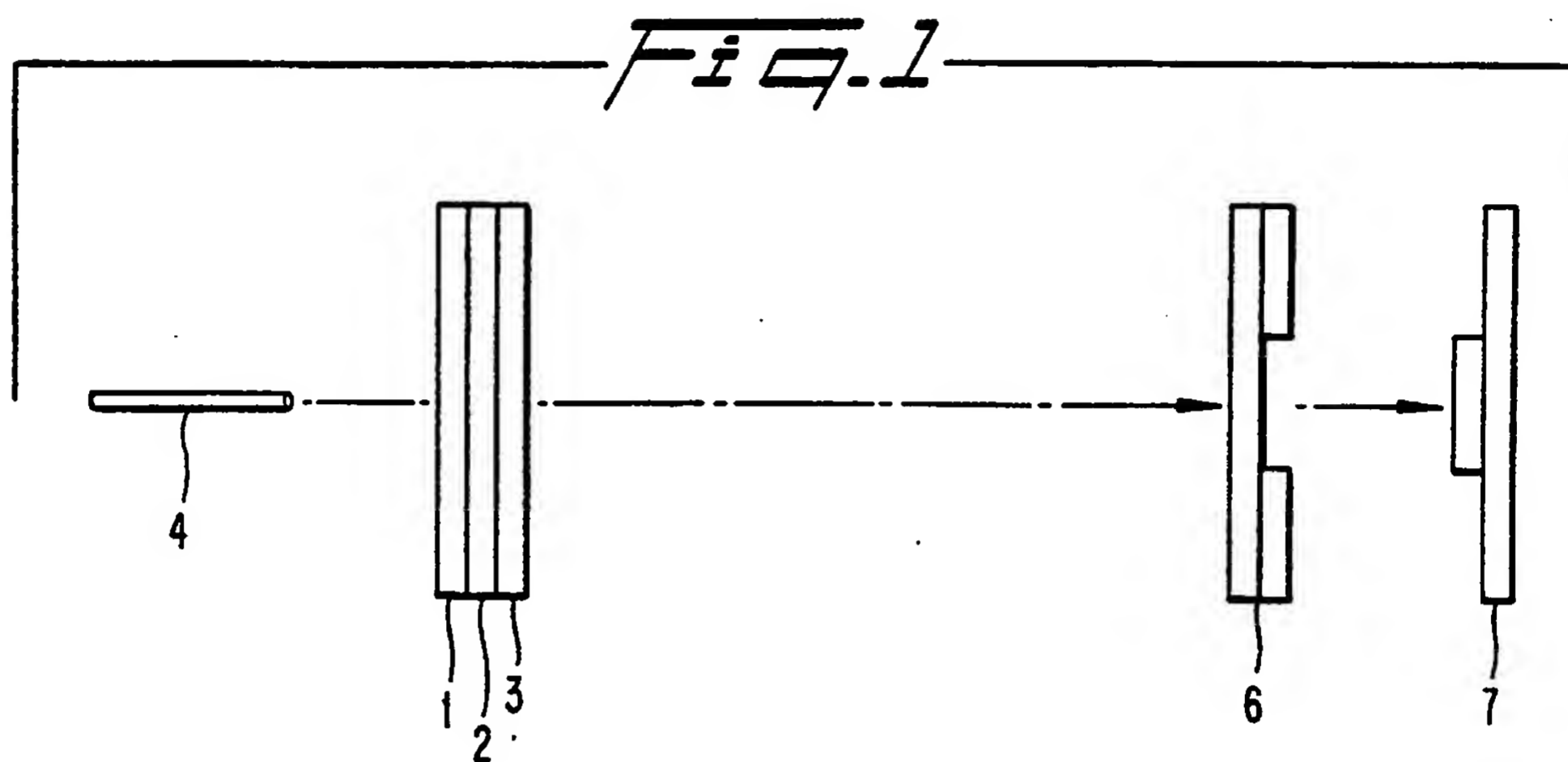
providing a color imaging donor material  
which comprises a support film having a near infrared  
10 absorbing layer thereon wherein said layer comprises a  
near infrared absorbing material, at least one  
decomposable binder and at least one material which is  
nonabsorbing at the desired near infrared wavelength  
and/or nondecomposing wherein the near infrared  
15 sensitive material consists essentially of at least  
one sensitizer which absorbs at a desired infrared  
wavelength for a particular laser output;

providing a receptor sheet positioned  
relative to the color imaging donor material in such a  
20 manner that it is effective in receiving material which  
has been ablated from the surface of the imaging donor  
material; and

introducing a laser output having the desired  
near infrared wavelength into the surface of the color

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imaging donor material so as to cause ablation of  
material from the surface of the coating onto the  
receptor sheet thereby forming both an imaged donor  
film and a color print or proof of reversed sign on the  
5 receptor sheet.



**SUBSTITUTE SHEET,**

# INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US90/01635**

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) <sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC  
**IPC G03C 1/492, G03C 1/00, G03C 5/00, G03C 7/00**  
**U.S. 430/270, 293, 358, 363, 495, 616**

## II. FIELDS SEARCHED

Minimum Documentation Searched <sup>7</sup>	
Classification System	Classification Symbols
U.S.	430/270, 293, 358, 363, 495, 616, 944, 945

Documentation Searched other than Minimum Documentation  
to the extent that such Documents are included in the Fields Searched <sup>8</sup>

## III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup>

Category <sup>*</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	US, A, 4,707,427 (TANAKA) 17 November 1987 See column 8 lines 3-20, column 10 claims 1&4	27-52
X,P	US, A, 4,857,431 (KATO) 15 August 1989 See column 2, lines 9-16, column 13, lines 66-68, and column 14, lines 1-6	1,4,6,8,10,12 17,19,27,30-39,41-44,79,82
X	US, A, 4,629,670 (KATAGIRI) 16 December 1986 Column 47 lines 5-18, column 79 claim 6	27-52,84-86 88
X	US, A, 4,634,652 (BARTON) 06 January 1987 Column 4 lines 59-68, column 5 lines 1-31	27-78,84-86 89
X	US, A, 4,514,493 (HIRAI) 30 April 1985 Column 14 claim 1	27-52,84-86 88
X	US, A, 4,725,519 (SUZUKI) 16 February 1988 See column 10 and 11 claims 1 and 2	27-52,84-86 88
X	US, A, 4,501,808 (SAKAI) 26 February 1985 See entire document	1-89
X	US, A, 4,551,413 (BELL) 05 November 1985 See column 21 claim 11,13 & 14	27-52,84-86 88

<sup>\*</sup> Special categories of cited documents: <sup>10</sup>

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

**03 MAY 1990**

Date of Mailing of this International Search Report

**06 AUG 1990**

International Searching Authority

**ISA/US**

Signature of Authorized Officer

*For Ashley I. Pezzner*  
**ASHLEY I. PEZZNER**

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE<sup>1</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers \_\_\_\_\_, because they relate to subject matter <sup>12</sup> not required to be searched by this Authority, namely:
  
2. ☐ Claim numbers \_\_\_\_\_, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out <sup>13</sup>, specifically:
  
3. ☐ Claim numbers \_\_\_\_\_, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING<sup>2</sup>

This International Searching Authority found multiple inventions in this international application as follows:

- I. Claims 1-26, 79-83, 87 drawn to a coating composition, class 430 subclass 616
- II. Claims 27-52, 84-86, 88 drawn to imaging material class 430 subclass 495
- III. Claims 53-78, 89 drawn to method providing color image class 430 subclass 293 (see attachment)

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application. Telephone Practice
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
  
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
  
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

(Continuation Sheet)

Reasons for lack of inventive entity

Invention I and invention II are related as a coating composition and imaging material. The inventions are distinct because invention II does not have to contain an aqueous solution.

Invention II and invention III are related as product and process of use. The inventions are distinct because the product can be used in optical recording as well as a color print of proof.